HYDROGEN-ISOTOPE CONSTRAINTS ON THE ORIGIN AND EVOLUTION OF THE CARBONACEOUS CHONDRITES. J.M. Eiler<sup>1</sup> Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125

**Introduction**: The carbonaceous chondrites are among the most primitive solid objects in the solar system and plausibly represent building blocks of the terrestrial planets, moons and asteroids [1,2]. though they are generally less differentiated and metamorphosed than other meteorite groups, the carbonaceous chondrites are compositionally and texturally diverse, in part reflecting processes acting on them after their accretion [3,4]. One of the more important of these processes was aqueous alteration, either by water formed from melting co-accreted ice or by infiltration of externally-derived water produced elsewhere on their meteorite parent bodies [5]. Several recent models of the protoliths, sources of water, and conditions and mechanisms of this water-rock reaction have been proposed based on evidence from oxygen isotope geochemistry [e.g., 6,7]. In this study, we re-examine this issue considering the added constraint of hydrogen isotope compositions of CV, CO, CM and CI carbonaceous chondrites. We particularly focus on the CM chondrites, which preserve the most diverse record of aqueous alteration.

Samples and methods: We present new measurements of hydrogen isotope compositions of mechanically micro-sampled portions of nine carbonaceous chondrites, including five CM chondrites (LEW 85311, Murchison, Mighei, Murray, Cold Bokkeveld), two CV chondrites (Allende and Mokoia) and two CI chondrites (Ivuna and Orgueil). We will also show data for Tagish Lake, although these are preliminary at present and not discussed in the following paragraphs. Three classes of materials were prepared from these samples: fragments of matrix, free of visible coarse crystalline material, veins or heterogeneities in color; central portions of large, aqueously altered chondrules; and aqueously altered loose fragments of coarse silicates (chondrules and/or CAI's).

All samples were analysed using a recently-developed method of on-line stepped combustion, reduction of evolved water, and continuous flow mass spectrometry of product H<sub>2</sub> [8]. This method reduces the sample size for hydrogen isotope analysis by ca. three to four orders of magnitude compared to conventional techniques, such that detailed stepped heating experiments can be conducted on tens to hundreds of micrograms of water-rich materials. Briefly, samples are loaded in a 1/8" O.D. alumina tube and dried for 12 hours at 50 °C under a He flow. A movable resistance heater is then slid over the portion of the alumina tube

holding the sample and heated in several steps over a period of  $\sim 30$  to 120 minutes. Water evolved from the sample tube into the He stream is cryogenically collected in a capillary of deactivated fused silica and periodically (every 2 to 5 minutes) purged through a reduction furnace (of either graphite and platinum or uranium filings) where it is converted to H<sub>2</sub>, which is swept into the source of a Finnigan Matt Delta-plus gas source mass spectrometer and HH $^+$  and HD $^+$  simultaneously detected as brief, time-varying signals.

Finally, we also re-evaluate previous conventional measurements of hydrogen isotope compositions (and other volatile-element properties) of whole-rock samples of a larger subset of CO, CV, CM and CI chondrites. These data demonstrate many of the same relationships between D/H and other geochemical properties observed in our micro-analytical measurements (although with greater scatter) and provide a means of generalising our results beyond the smaller group of nine samples studied in detail here.

Results and Discussion: Hydrogen isotope compositions of CM chondrite matrix and whole-rocks decrease monotonically with increasing degree of aqueous alteration, as inferred from petrography, mineral chemistry and oxygen isotopes [5, 6]. The least altered extreme to this trend has matrix and whole-rock δD<sub>SMOW</sub> values near 0 ‰, whereas the most altered extreme has values near -200 ‰. Correlations of matrix and whole-rock δD values vs. various oxygen isotope indices ( $\Delta^{17}$ O; [ $\delta^{18}$ O<sub>matrix</sub> —  $\delta^{18}$ O<sub>whole rock</sub>]; e.g., Figures 1a,b) are linear rather than sharply hyperbolic as expected for reaction between water and initially Hpoor rocks like the CV and CO chondrites. Altered chondrule cores and coarse silicate fragments are systematically lower in  $\delta D$  than co-existing matrix. The 'cleanest' (most matrix-free) samples of these coarse materials all have δD values near -200 per mil, independent of the extent of aqueous alteration of their host rocks. These data document the importance of waterrock reaction for controlling the D/H ratio of CM chondrites, constrain the D/H ratio of both the CM chondrite protoliths and infiltrating water, and suggest that the matrix of the protoliths of CM chondrites was H-rich before infiltration by low-D/H water (i.e., such that both H and O isotope compositions of matrix and whole rock change gradually with increasing extent of water-rock reaction). If so, the H-poor CO and CV chondrites cannot be protoliths of the CM chondrites, as suggested by oxygen isotopes alone [6,7].

Matrix and whole-rocks from CI chondrites are uniformly higher in  $\delta D$  (+100±20 ‰, n=5 for our measurements) than matrix, whole-rocks or altered coarse silicates in CM chondrites. Thus, while the CI chondrites are similar in oxygen isotope composition to the most altered CM chondrites (e.g., Nogoya; Cold Bokkeveld), they are systematically ca. 300 per mil higher in  $\delta D$  than those rocks. This result is inconsistent with the CI chondrites being more altered versions of the CM chondrites, as suggested by some models based on oxygen isotopes alone (e.g., [7]; note, however, that this relationship was not implied in the model of [6]). More significantly, the CI and CM chondrites do form continuous trends in plots of  $\delta D$  vs. other geochemical properties, but only when the other variable involves highly or moderately volatile elements. The sense of these trends is opposite those one might infer from models based on oxygen isotopes alone [7]. In particular, the CI and CM chondrites define trends of decreasing abundances of highly and moderately volatile elements (e.g., N, C, Na, <sup>36</sup>Ar) with decreasing δD (e.g., Figure 2). In all such trends, CI chondrites are the high- $\delta D$ , volatile-rich extreme, and CM chondrites gradually diverge from this extreme toward lower  $\delta D$  values and volatile contents with increasing extents of aqueous alteration (i.e., increasing water-rock reaction makes the CM chondrites less like, rather than more like, the CI chondrites in these properties). This result is consistent with the protolith of the CM chondrites being a mixture of sub-equal amounts of highly volatile-rich matrix (much like the CI chondrites) on one hand and volatile-poor chondrules and other coarse, anhydrous phases on the other—i.e., it was a C2 chondrite having volatileelement abundances and isotope ratios resembling the C1 chondrites. This conclusion is consistent with our inference in the preceding paragraph that the CM chondrite protolith was far richer in H than the CO or CV chondrites. No rock closely resembling our inferred CM chondrite protolith is recognised in meteorite collections, although the Tagish Lake meteorite is perhaps the closest analogy.

We estimate that the water that infiltrated the CM chondrites had a  $\delta D$  value of -150 ‰, similar to that predicted for ices accreted at 4 AU ca. 1 million years after initial collapse of the pre-solar nebula [9].

**References:**[1] Anders E and Grevesse N (1989) *GCA*, 53, 197-214. [2] MacPherson GJ et al. (1988) *Meteorites and the Early Solar System*, p. 746-807. [3] VanSchmus WR and Wood JA (1967) *GCA*, 31, 747-765. [4] McSween HY (1979) *RGSS*, 17, 1059-1078. [5] Browning LB et al. (1996) *GCA*, 60, 2621-2633. [6] Clayton RN and Mayeda TK (1999) *GCA*, 63, 2089-2104. [7] Young ED et al. (1999) *Science 286*,

1331-1335. [8] Eiler JM and Kitchen N (2001) *GCA*, 65, 4467-4479. [9] Morbidelli A et al. (2000) *MPS*, 35, 1309-1320.

Figure 1a: matrix and chondrules from CM chondrites

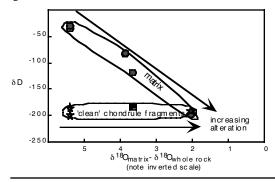


Figure 1b: whole-rock samples of CM chondrites

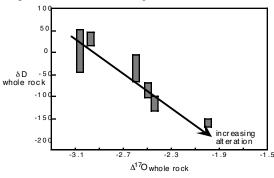


Figure 2: whole-rock samples of CM and CI chondrite

